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THE SCHMIDT REACTION ON CAMPHOR. UNUSUAL FORMATION OF A UREA.

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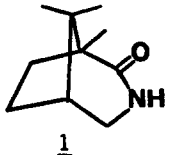
During the course of some investigations of N-Nitrosamine photolysis we attempted to prepare α-camphidone 1 via the Schmidt reaction on camphor. We rejected the alternate Beckmann route since cleavage products appear to predominate from that reaction (1,2). Schmidt isolated tetrazole 2 from the action of hydrazoic acid on camphor (3).

Camphor proved to be relatively stable to a variety of reaction conditions (4,5), however, reaction in chloroform - sulfuric acid with sodium azide (2.2 equivalents) yielded less than 1% of 1 (6) together with about 30% of the urea 3 m.p. 178-180°, and unchanged camphor (65%). The structure of 3 follows from elemental analysis ($C_{10}H_{18}N_2O$); mass



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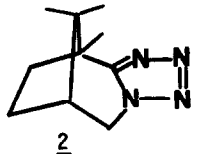

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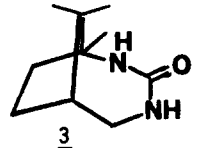

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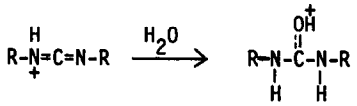
spectrometry (M^+ 182, m/e 167 $[M^+ - CH_3]$, m/e 139 $[M^+ - HNCO]$); infrared spectroscopy (ν_{max} 3200, 3150 and 1650 cm^{-1}) (7); ultraviolet spectroscopy (λ_{max} 210 nm ε 3410) (8), n.m.r. and hydrolysis to the corresponding diamine (isolated as the hydrochloride).

Urea formation during the Schmidt reaction on ketones has been observed before (9) but the proposed intermediate was the protonated carbodiimide 4. This seems an unlikely route



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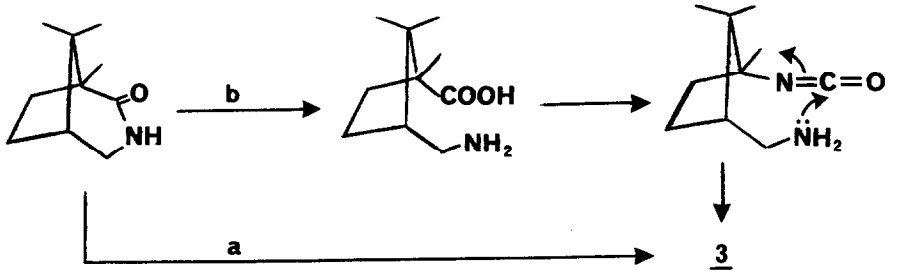
in the case of camphor, the linear carbodiimide system being impossible to accommodate in the ring system. Two possible routes to 3 seem feasible: a) a second Schmidt reaction on

α-camphidone (7). b) opening of α-camphidone to an amino acid followed by Schmidt reaction to an amino-isocyanate and ring closure (10) (Scheme). Our synthetic routes to 3 are based along these lines.



Scheme. Possible routes to urea 3

Acknowledgement

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